Analytical Boltzmann Moments for Electrons in N_2-O_2-H_2O Gas Mixtures

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The Boltzmann equation for the electron energy distribution function in weakly ionized N_2-O_2-H_2O gas mixtures with uniform electric fields is solved by an approximate analytical procedure. This work supports a plasma de-NO_x experimental project. Prior work has shown that when the Boltzmann equation is reformulated for the logarithmic derivative of the distribution function that it can be solved quickly by numerical iteration. Approximate analysis of the inelastic collision integrals used in the iterative approach yields a closed form for the distribution function that helps speed numerical convergence. By using this analytical approximation, and additional modeling of actual electron-molecule cross sections as locally constant within sequential energy intervals, we can integrate the moments of the Boltzmann equation and write explicit formulas for the average electron velocity, energy, the drift velocity, and dissociation rate coefficients as functions of E/N and species fractional concentrations. Examples for various mixtures are presented over the E/N range of 10 to 1000 Td. Some comparisons with experiment and other work are included.

Non-equilibrium gas plasmas are under study today as sources of electrically powered chemistry for the elimination of volatile organic vapors and combustion exhaust pollutants. The energy of an imposed electric field is transferred by electrons into molecular excitation and dissociation. Radical oxidizing species like O, OH, and O_3 are formed from molecular oxygen and water in air for example, while reducing agents like H and N atoms are produced from the water and molecular nitrogen. The aim of these research efforts is to develop either non-catalytic oxidation to acids which can be "scrubbed" out of gas flows as salts, or non-catalytic reduction, specifically of NO_x to N_2 and O_2.

Electron kinetics in slightly ionized molecular gas mixtures are dominated by inelastic collisions and are inherently non-equilibrium. The non-Maxwellian electron distribution function is determined by solving the Boltzmann equation for a specific mixture at a specific Townsend parameter (the ratio of electric field to total number density, E/N, where 1 Td $=10^{-17}$ Volts-cm^2). Given this, dissociation rate coefficients are calculated by taking velocity moments over the appropriate electron-molecule cross sections. The myriad interactions possible between the electrically generated radical, atomic and excited species with the original molecular components has spurred the development of chemical kinetics models with as many as three hundred reactions.

Our work is an effort to simplify the electron kinetics so as to enable a convenient study of a wide range of mixtures and Townsend parameters, and for a reasonable sacrifice in precision. Key insights gained in this way can be honed by more accurate numerical computation as needed.

In this report we present a brief description of our approximate analytical solution of the Boltzmann equation, then additional modeling of electron-molecule cross sections which simplifies the expressions for moments, and finally a number of examples and comparisons to experiment and published results.

List of Symbols:

$f(\varepsilon)$ □   electron energy distribution function

$\dfrac{E}{N}$ □   ratio of the electric field to the total number density

δ_i^s □   fractional concentration of species s at energy state i

$Q_m^s(\varepsilon)$ □   electron-molecule momentum transfer cross section for species s

$S_{ij}^s(\varepsilon)$ □   electron-molecule inelastic cross section for a transition from state i to state j of species s

ε_{ij}^s □   the energy exchange for transition i to j of species s

T_v^s □   the vibrational temperature of species s

Indices denote the following: (s: species), (i, j: states involved in a transition), (n: vibrational transitions of n levels), and (x: electronic, dissociative, ionization excitations)

Boltzmann Equation:

$$-\frac{\left[\dfrac{E}{N}\right]^2}{3}\cdot\frac{\varepsilon}{\displaystyle\sum_s \delta^s \cdot Q_m^s(\varepsilon)}\cdot\frac{df(\varepsilon)}{d\varepsilon} = 0$$

$$\sum_s\sum_i\sum_j \delta_i^s \cdot \int_\varepsilon^{\left[\varepsilon+\varepsilon_{ij}^s\right]} \xi S(\xi)_{ij}^s \cdot f(\xi)\,d\xi = 0$$
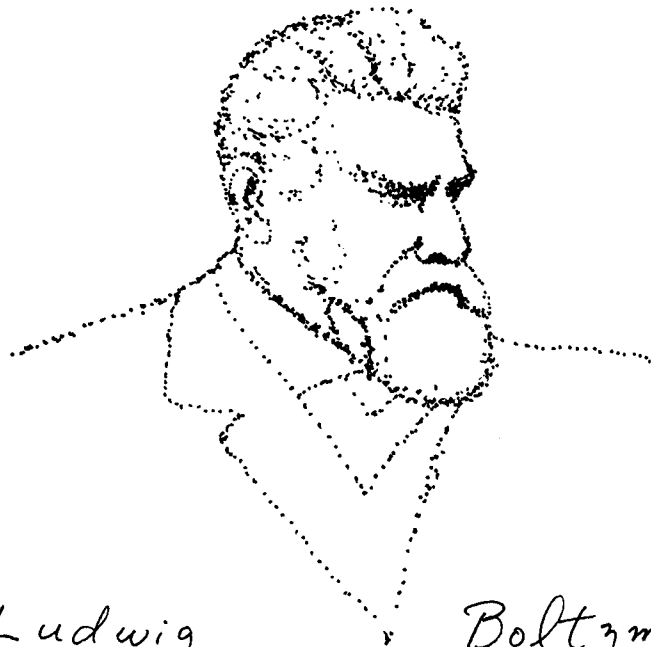
Ludwig Boltzmann
1844 - 1906

Logarithmic derivative:

$$B(\varepsilon) := \frac{-d\ln f(\varepsilon)}{d\varepsilon} \quad \Box \qquad\qquad \mu(\varepsilon) := \frac{\left[\dfrac{E}{N}\right]^2}{3} \cdot \frac{\varepsilon}{\sum\limits_{s} \delta^s \cdot Qm(\varepsilon)^s} \quad \Box$$

Boltzmann Equation:

$$\mu(\varepsilon) \cdot B(\varepsilon) = \quad \Box$$

$$\sum_{s} \sum_{j > i} \int_{\varepsilon}^{\left[\varepsilon + \varepsilon_{ij}^s\right]} \left[\delta_i^s \cdot e^{\int_{\xi}^{\varepsilon} B(n)\,dn} \quad \cdots \quad + -\delta_j^s \cdot e^{\int_{\xi - \varepsilon_{ij}^s}^{\varepsilon} B(n)\,dn} \right] \cdot \xi \cdot S(\varepsilon)_{ij}^s \, d\xi \quad \Box$$

Simplifications:

1) **Maxwellian gas populations:**

$$\delta_i^s := \delta^s \cdot e^{-\left[\dfrac{\varepsilon_i^s \cdot e}{kT_v^s}\right]} \qquad \square$$

$$\sum_s \sum_i \delta_i^s := 1 \qquad \square$$

2) **harmonic vibrational levels:**

$$\varepsilon_{ij}^s := (j - i) \cdot \varepsilon_{01}^s \qquad \square$$

$$S(\varepsilon)_{ij}^s := S(\varepsilon)_{j-i}^s \qquad \square$$

3) **superelastic collisions from detailed balance:**

$$\left[\varepsilon + \varepsilon_{ij}^s\right] \cdot S\left[\varepsilon + \varepsilon_{ij}^s\right]_{ij}^s := \varepsilon \cdot S(\varepsilon)_{ji}^s \qquad \square \qquad j > i \qquad \square$$

4) slow variation of cross sections above threshold:

$$\sum_{\text{vibration}} S(\zeta)_n^s \approx \sum_n S\left[\varepsilon + \frac{\varepsilon_{01}^s}{2}\right]_n^s \quad \square$$

$$\varepsilon \le \zeta \le \varepsilon + \varepsilon_{01}^s \quad \square$$

5) slow variation of B(ε) above cross section thresholds:

$$\int_{\varepsilon}^{\varepsilon + \varepsilon_{01}^s} B(\eta)\, d\eta \approx B(\varepsilon) \cdot \left[\varepsilon_{01}^s\right] \quad \square$$

6) vibrational temperatures are moderate:

$$\sigma_1^s \equiv e^{-\left[\left[\varepsilon_1^s - \varepsilon_0^s\right] \cdot \dfrac{e^s}{kT_v^s}\right]} \quad \square \qquad\qquad \sigma_i^s \approx 0 \quad \square$$
$$i > 1$$

Approximate equation for B:

$$\mu(\varepsilon) \cdot B(\varepsilon) := \square$$

$$\sum_{s} \delta_s \cdot \int_{\varepsilon}^{\varepsilon + \varepsilon_{01}^{s}} \left[B \cdot e^{(\varepsilon - \xi)} \quad \cdots \quad \begin{array}{c} \\ + \, -\sigma_s \cdot e^{B \cdot \left[\varepsilon - \xi + \varepsilon_{01}^{s}\right]} \\ 1 \end{array} \right] \cdot \xi \cdot S(\xi)_{v}^{s} \, d\xi \ \square$$

for vibration use: $\quad S(\xi)_{v}^{s} \equiv \sum_{n} S(\xi)_{n}^{s} \ \square$

A similar formalism applies for the electronic, dissociation and ionization terms of the equation for $B(\varepsilon)$ by use of the appropriate cross sections $S(\xi)$ and energy losses $\Delta\varepsilon$.

Algebraic equation for $B(\varepsilon)$:

$$\mu(\varepsilon)\cdot B(\varepsilon) \ := \ \Box$$

$$\sum_s \delta^s \cdot \left[1 - \sigma_1^s \cdot e^{\displaystyle B(\varepsilon)\cdot\varepsilon_{01}^s} \right] \cdot S(\zeta)_v^s \cdot K\left[\varepsilon, B(\varepsilon), \varepsilon_{01}^s\right] \ \Box$$

where:

$$K\left[\varepsilon, B(\varepsilon), \varepsilon_{01}^s\right] := \frac{B\cdot\varepsilon + 1 - \left[B\cdot\left[\varepsilon + \varepsilon_{01}^s\right] + 1 \right]\cdot e^{-\left[B\cdot\varepsilon_{01}^s \right]}}{B^2} \ \Box$$

This result was obtained by G. K. Bienkowski (1975).

Zeroth Iterant:

The algebraic equation for B(ε) can be solved by further analytical simplification or by numerical iteration. The resulting B(ε) is an excellent initial estimate for an iterative solution of the full integro-differential equation for the logarithmic derivative of f(ε), (Garcia & Bienkowski, 1975). Bienkowski developed a scaling law for inelastic electron-molecule energy transfer in mixtures, and computed accurate f(ε) functions on the basis of the algebraic equation for B(ε).

Further simplification of the algebraic equation follows:

$$B(\varepsilon) \approx Order(1) \quad \square$$

$$B(\varepsilon) < \frac{e}{\underset{v}{\underset{kT}{s}}} \quad \square \qquad \text{for problems of interest.}$$

(B is like a local inverse temperature, for a Maxwellian B = e/kT$_e$)

$$K\left[\varepsilon, B(\varepsilon), \varepsilon^{s}_{01}\right] \approx \frac{\varepsilon}{B(\varepsilon)} \quad \square$$

The analytical approximation for B(ε) follows:

Analytical approximation:

$$f(\varepsilon) := \cfrac{e^{-\int_0^\varepsilon B(n)\,dn}}{\displaystyle\int_0^{00} e^{-\int_0^\varepsilon B(n)\,dn}\cdot\sqrt{\varepsilon}\,d\varepsilon} \qquad \Box$$

$$B(\varepsilon) := \qquad \Box$$

$$\sqrt{\cfrac{3\cdot\left[\displaystyle\sum_s{}^s \delta^s\cdot Qm(\varepsilon)^s\right]\cdot\left[\displaystyle\sum_s{}^s \delta\cdot\left[\left[1-\sigma\begin{matrix}s\\1\end{matrix}\right]\cdot S(\varepsilon)^s{}_v \dots + \displaystyle\sum_x{}^s S(\varepsilon)^s{}_x\right]\right]}{\cfrac{E}{N}}} \qquad \Box$$

Model Calculations

Calculating the average electron velocity, energy, drift velocity (for current flow), and collisional rate coefficients (such as for dissociation) requires the integration of products that include $f(\varepsilon)$ and the cross sections. The examples which follow show the application of the analytical approximations for $B(\varepsilon)$ and $f(\varepsilon)$ in conjunction with simple models of cross sections which enable these integrations to be performed analytically. This results in explicit formulae for moments which depend only on E/N and a number of constants specified by the nature of the mixture (fractional concentrations and cross sections).

We consider mixtures of molecular nitrogen, oxygen and water. Cross sections are modeled as locally constant within a sequence of adjacent energy intervals. Ten intervals with edges at 0, 0.5, 1.5, 1.7, 3.2, 4, 5.1, 9.7, 22, 30, and 100 eV were chosen. Within each of these intervals (index i) a constant B_i was developed on the basis of the analytical approximation. An important feature of the analysis is that $B_i = q_i/(E/N)$, where each q_i equals the square root of the product of momentum transfer and excitation cross sections appropriately weighted by mixture ratios. In this way the q_i can be determined once for a given mixture and utilized to determine the B_i and the moments for any E/N in that mixture.

The distribution function within any interval i appears like a segment of a Maxwellian with a temperature $1/B_i$. This enables moments to be integrated analytically within each interval and each moment then comprises of a summation of ten elements. We will state the moment equations based on this interval model.

All our examples here are calculated on the basis of the interval model cross section set shown as a three part figure (top to bottom: nitrogen, oxygen, water; log-log plots; upper/lower lines: momentum transfer/net inelastic, cm^2 vs. eV). Given the model's simplicity its agreement with reality is reasonable, especially between 30 to 300 Td and 2 to 12 eV where dissociation and ozone formation occur.

Terms used in moment equations:

$B_i :=$ ▫   analytical approximation to the logarithmic derivative of $f(\epsilon)$ within interval i, of form:

$$B_i := \frac{\sqrt{3 \cdot Qm \cdot S_x}}{\dfrac{E}{N}} \ ▫$$

$b_i :=$ ▫   upper edge of interval i (starting with 0 for i=0, and examples here use ten intervals with upper edges 0.5, 1.5, 1.7, 3.2, 4, 5.1, 9.7, 22, 30, 100)

$$\beta_i := \left[-b_{i-1} \cdot B_i + \sum_{j} \left[b_j - b_{j-1} \right] \cdot B_j \right] \ ▫$$

$$j := 1,2 \ ..(i - 1) \ ▫$$

Interval model moment equations

for intervals: $i := 1, 2 \ .. 10$ □

normalization:

$$C := \int_{0}^{00} f(\varepsilon) \cdot \sqrt{\varepsilon} \ d\varepsilon \ \square$$

$$C := \sum_{i} \frac{e^{-\beta_i}}{B_i^{\frac{3}{2}}} \cdot \int_{B_i \cdot b_{i-1}}^{B_i \cdot b_i} \sqrt{x \cdot e^{-x}} \ dx \ \square$$

$$C \approx \frac{1}{2} \cdot \sum_{i} e^{-\beta_i} \cdot \left[b_i - b_{i-1} \right] \cdot \left[\sqrt{b_i} \cdot e^{-\left[B_i \cdot b_i \right]} \ \cdots \ + \sqrt{b_{i-1}} \cdot e^{-\left[B_i \cdot b_{i-1} \right]} \right] \ \square$$

average energy:

$$\varepsilon_e := \frac{1}{C} \cdot \sum_i \frac{e^{-\beta_i}}{B_i^{\frac{5}{2}}} \cdot \int_{B_i \cdot b_{i-1}}^{B_i \cdot b_i} x^{\frac{3}{2}} \cdot e^{-x} \, dx \quad \square$$

$$\varepsilon_e \approx \frac{1}{2 \cdot C} \cdot \sum_i e^{-\beta_i} \cdot \left[b_i - b_{i-1} \right] \cdot \begin{bmatrix} b_i \cdot e^{\frac{3}{2} - \left[B_i \cdot b_i \right]} & \cdots \\ & \\ + b_{i-1} \cdot e^{\frac{3}{2} - \left[B_i \cdot b_{i-1} \right]} & \end{bmatrix} \quad \square$$

define W_i for use in velocity & rate moments:

$$W_i := \left[\left[B_i \cdot b_{i-1} + 1 \right] \cdot e^{-\left[B_i \cdot b_{i-1} \right]} - \left[B_i \cdot b_i + 1 \right] \cdot e^{-\left[B_i \cdot b_i \right]} \right] \quad \square$$

average velocity and collision rates:

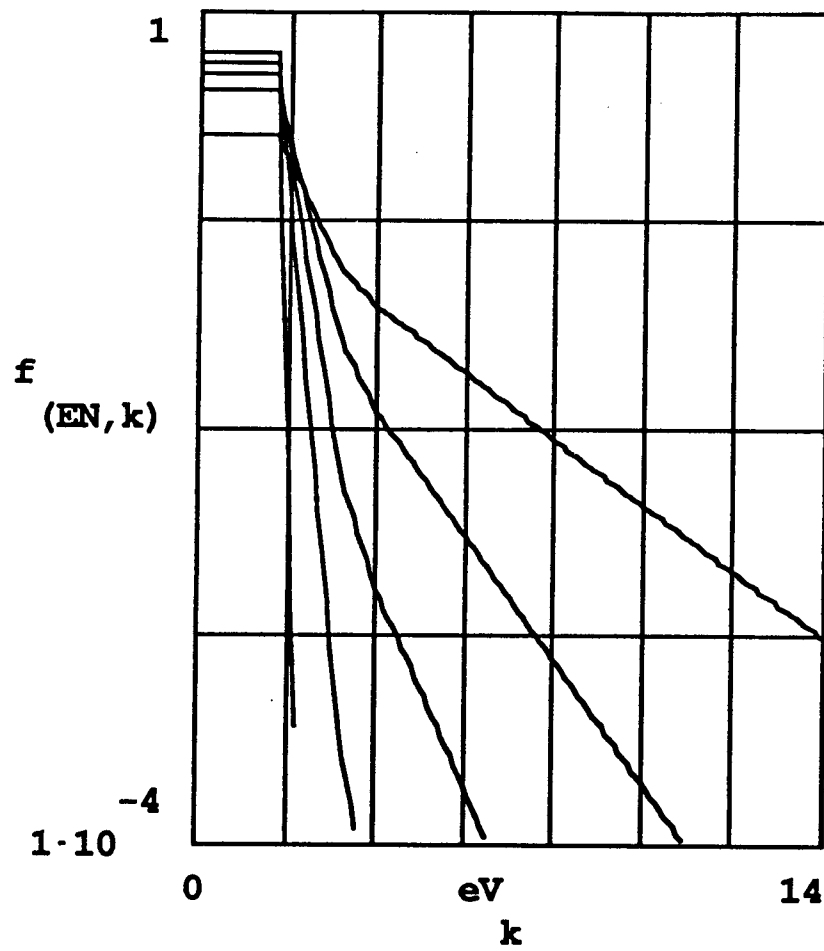$$v_e := \sqrt{2 \cdot \frac{e}{m} \cdot \frac{1}{C} \sum_i \frac{e^{-\beta_i}}{B_i^2} \cdot W_i} \quad \Box$$

$$v_{drift} := \sqrt{2 \cdot \frac{e}{m} \cdot \frac{N \cdot \frac{E}{-}}{3 \cdot C} \cdot \sum_i \frac{e^{-\beta_i}}{Qm_i \cdot B_i} \cdot W_i} \quad \Box$$

$$k_x := \sqrt{2 \cdot \frac{e}{m} \sum_{ix} \frac{S_{ix}}{C_{ix}} \cdot \frac{e^{-\beta_{ix}}}{B_{ix}^2} \cdot W_{ix}} \quad \Box$$

summation over ix intervals spanned by x process

Plot 1:
$3 \cdot 10^{-15}$

QNm_i , QNx_i

$3 \cdot 10^{-17}$

.1   e   100

i

Plot 2:
$1 \cdot 10^{-15}$

QOm_i , QOx_i

$1 \cdot 10^{-18}$

.1   e   100

i

Plot 3:
$1 \cdot 10^{-14}$

QWm_i , QWx_i

$1 \cdot 10^{-17}$

.1   e   100

i
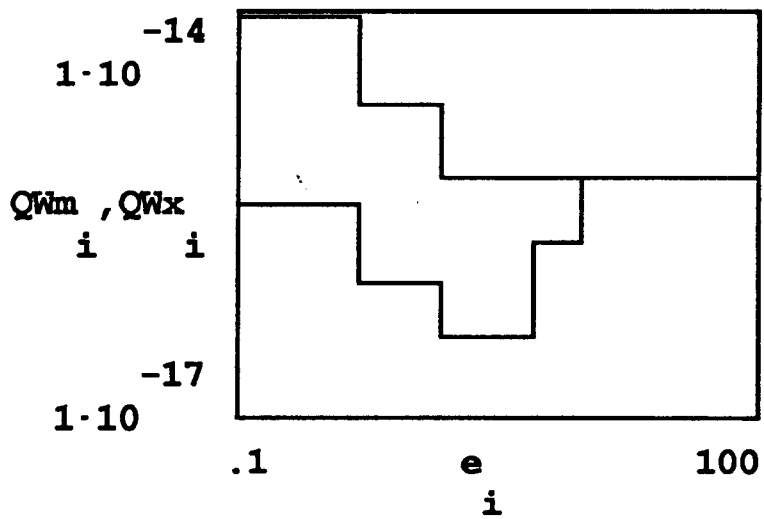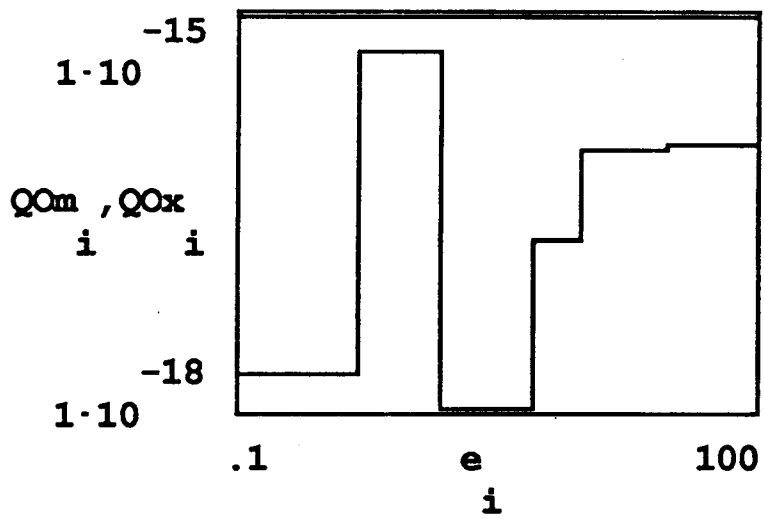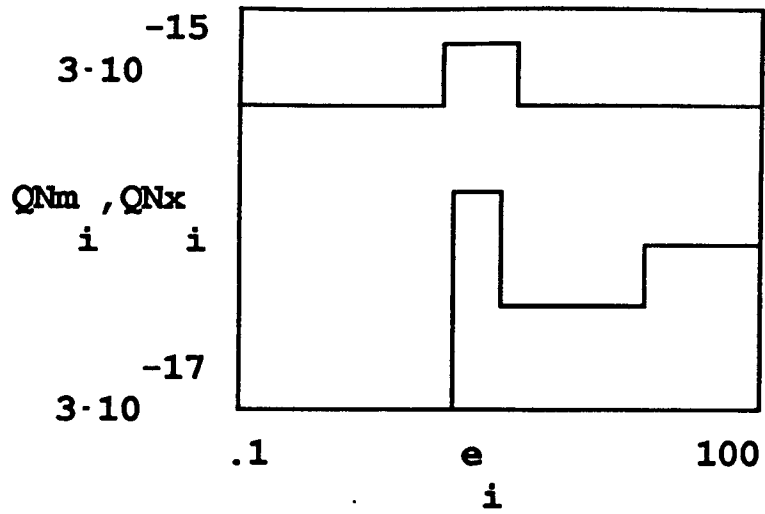
Electron distribution function

| $\delta N = 1$ | Nitrogen fractional concentration |
| $\delta = 0$ | Oxygen fractional concentration |
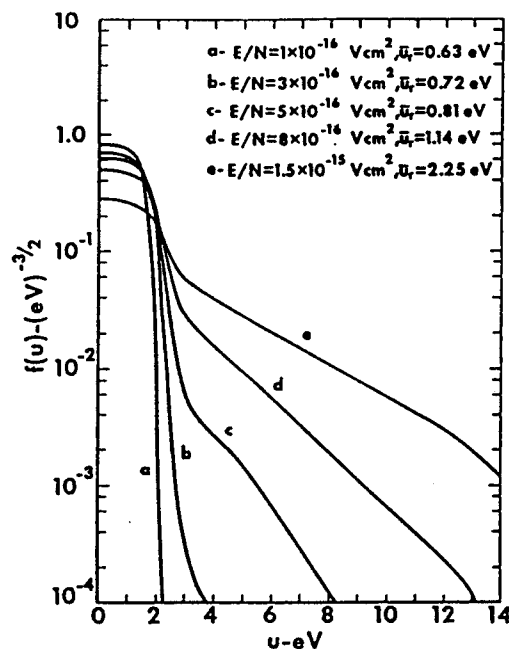
FIG. 1. Electron energy distribution functions in N_2 for various E/N values. The distribution function is defined such that $\int_0^\infty u^{1/2} f(u)\,du = 1$ and the reduced average energy such that $\bar{u}_r = \frac{2}{3} \int_0^\infty u^{3/2} f(u)\,du$.

Electron Energy Distributions and Collision Rates in Electrically
Excited N_2, CO, and CO_2[†]

William L. Nighan
United Aircraft Research Laboratories, East Hartford, Connecticut 06108
(Received 22 June 1970)
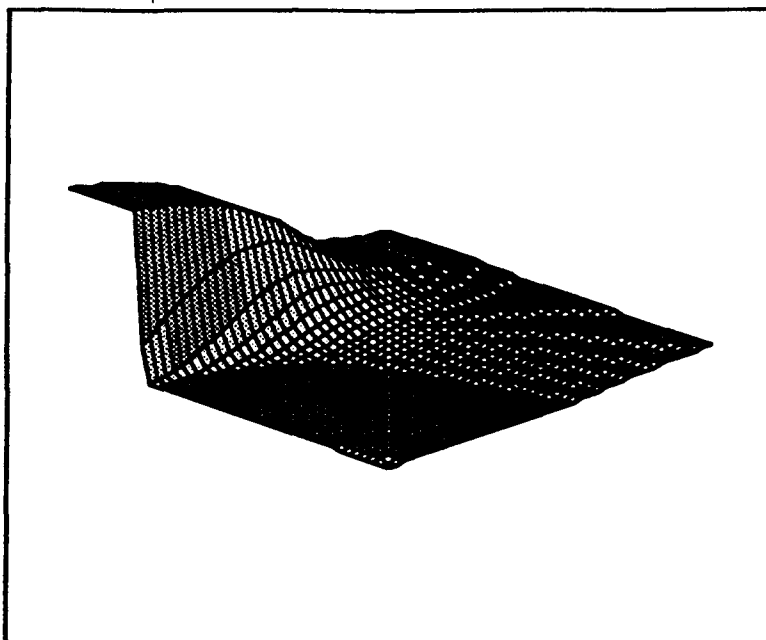
ELECTRONS
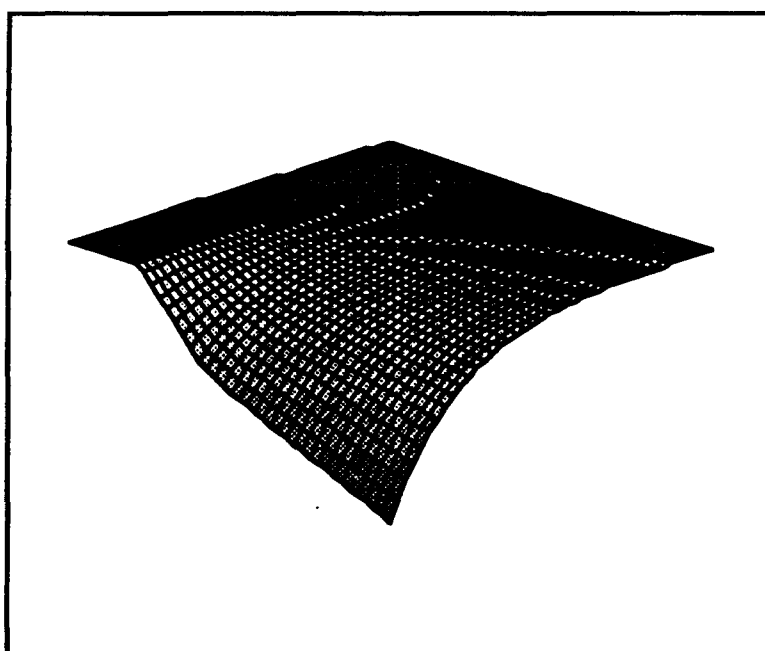
LOGtrons

Electron distribution between 0 - 8 eV, and 10 - 1000 Td

$\delta N = 1$ Nitrogen fraction

$\delta = 0$ Oxygen fraction

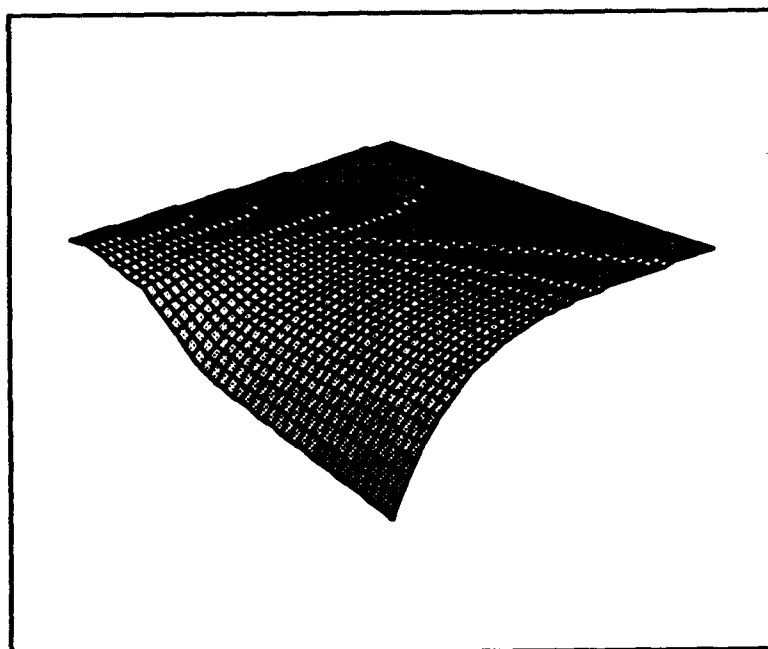# Electron distribution function
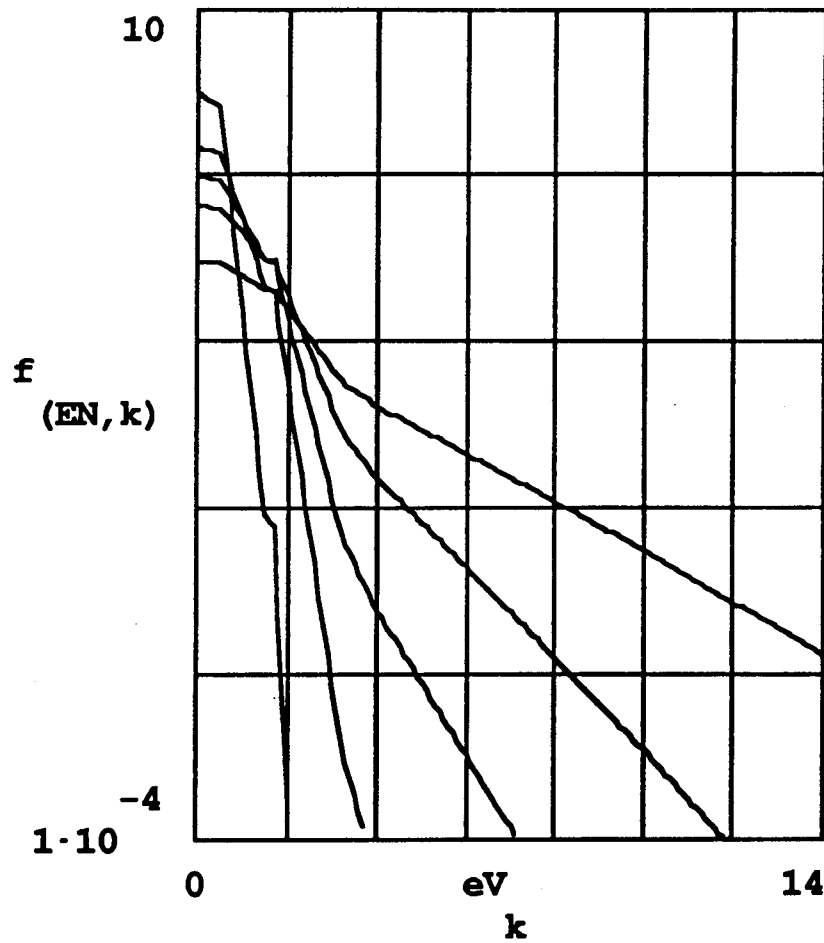
$\delta N = 0.79$ Nitrogen fractional concentration

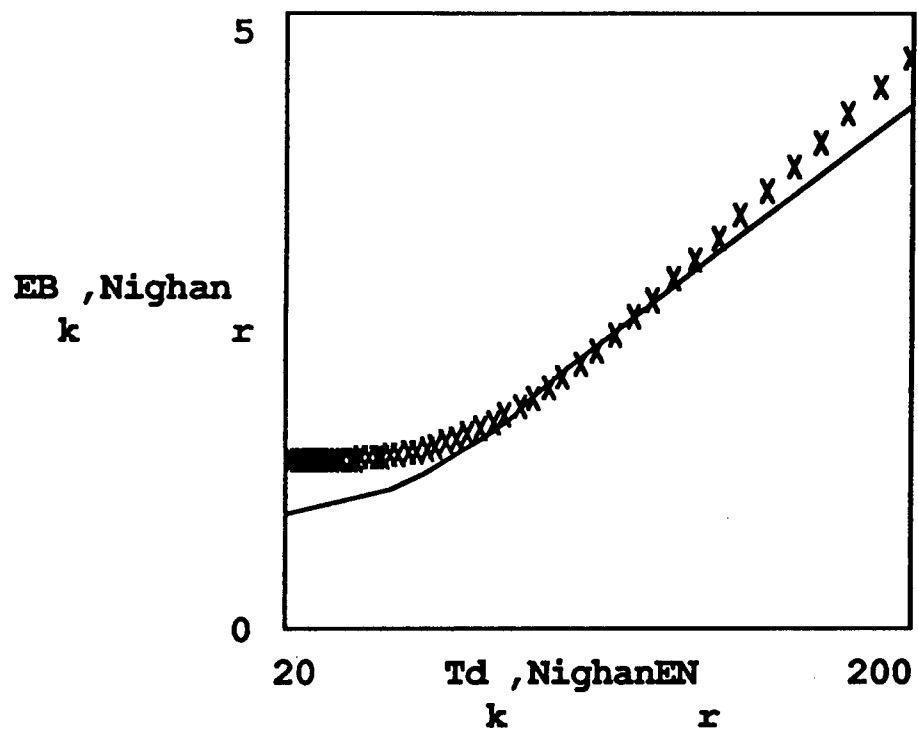$\delta = 0.21$ Oxygen fractional concentration
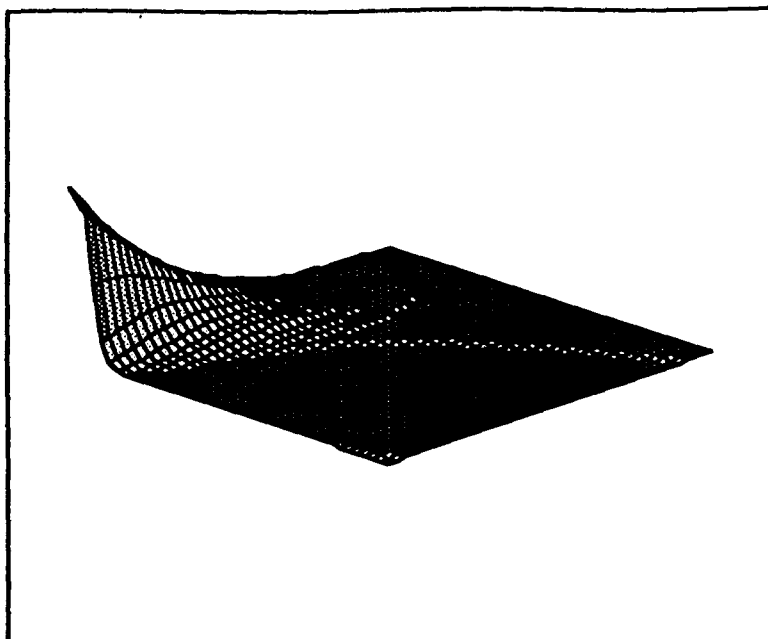
ELECTRONS

LOGtrons

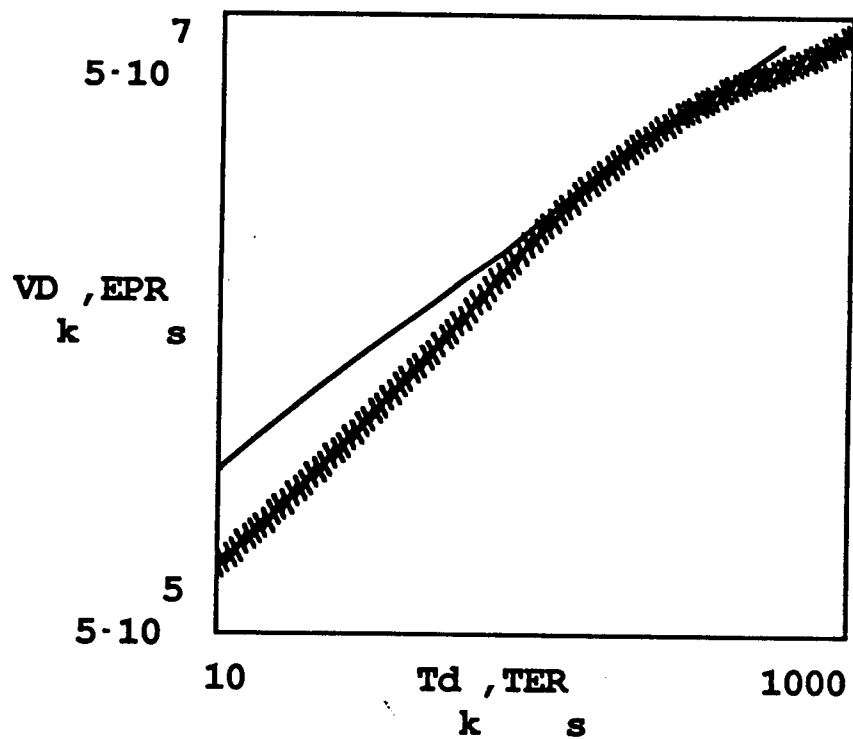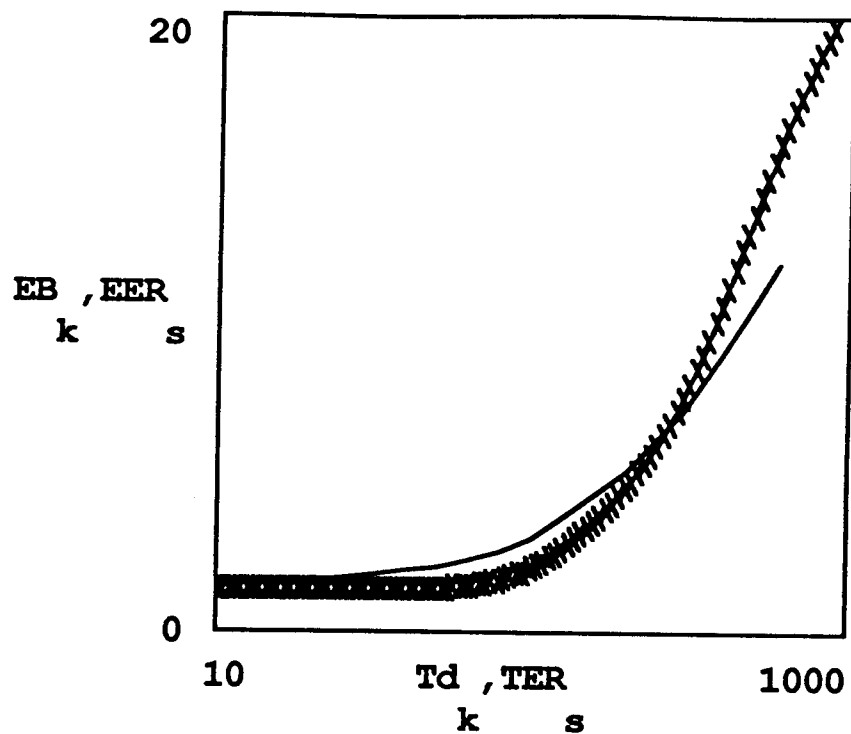Electron distribution between 0 - 8 eV, and 10 - 1000 Td

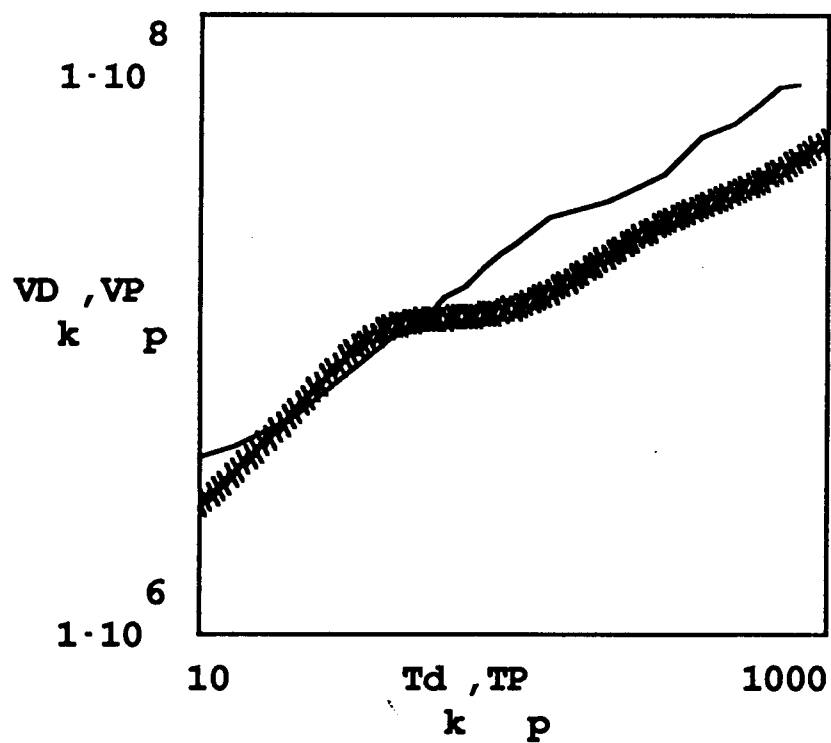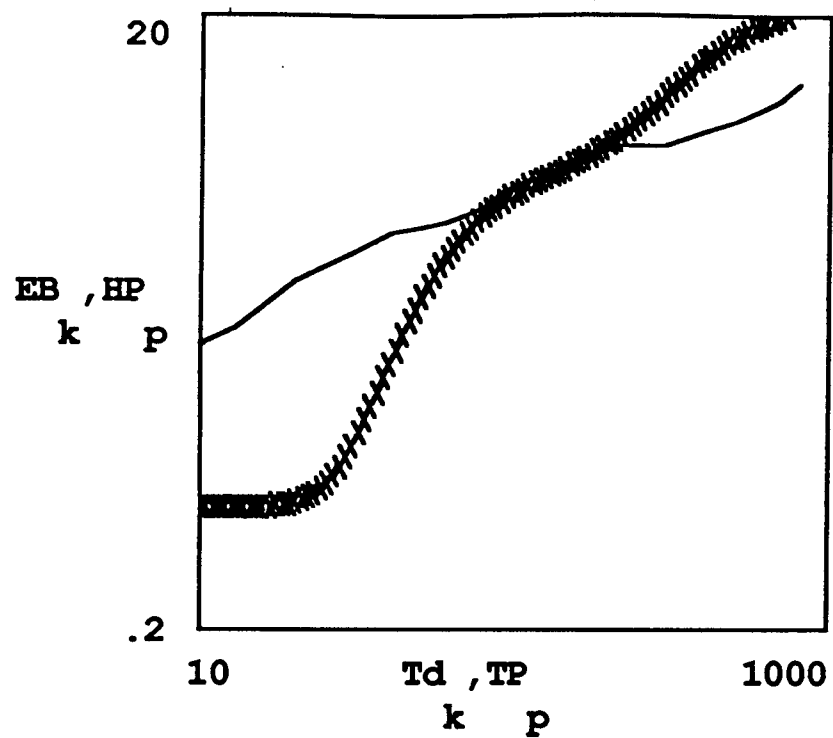δN = 0.79 Nitrogen fraction

δ = 0.21 Oxygen fraction

Electron average energy @ E/N in Nitrogen (line: Nighan, 1970)

eV (linear) vs. Townsends (logarithmic)

EB_k , EER_s

20

0

10 Td_k , TER_s 1000

7

$5 \cdot 10$

VD_k , EPR_s

5

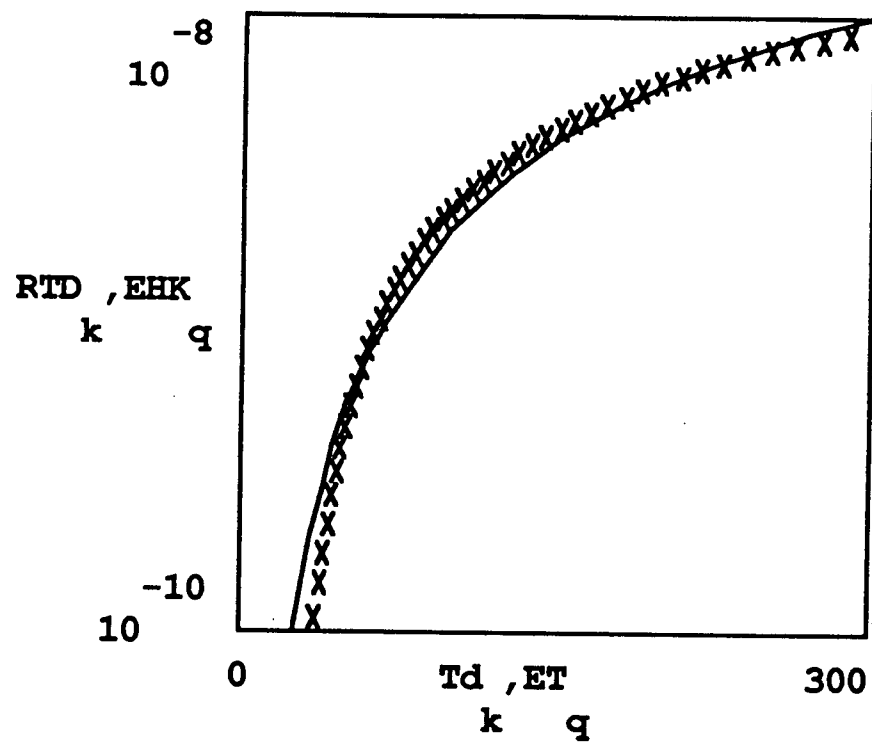$5 \cdot 10$

10 Td_k , TER_s 1000

Average energy & drift velocity in N2 (lines: Engelhardt, 1964)

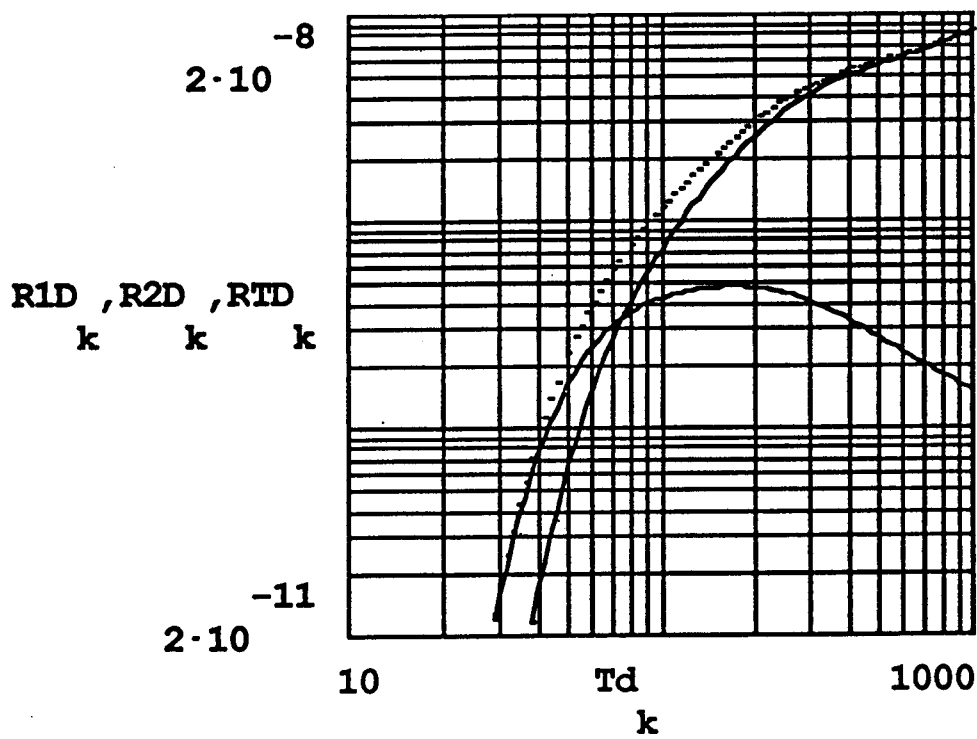eV & cm/s vs. Townsends (linear-log, & log-log)

Average energy & drift velocity in O2 (lines: Hake & Phelps, 1967)
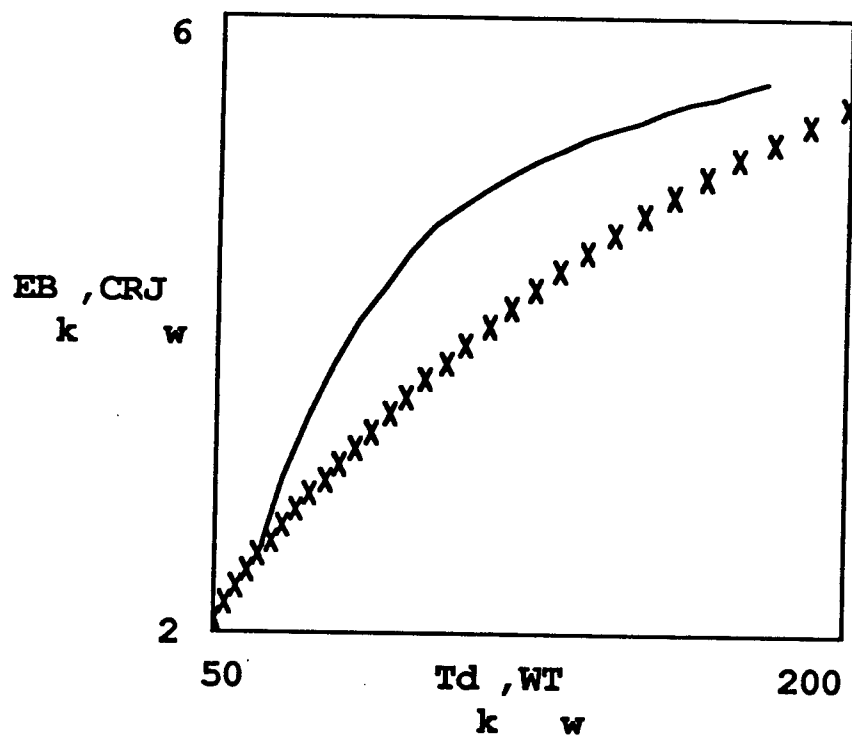
eV & cm/s vs. Townsends (log-log)

10^{-8}

RTD ,EHK
k   q

10^{-10}

0   Td ,ET   300
         k   q

Oxygen dissociation rate @ E/N in pure O2 (line: Eliasson, 1987)

cc/s (logarithmic) vs. Townsends (linear)

$1 \cdot 10^{-0}$

OZONE
k

$1 \cdot 10^{-3}$

10   Td   1000
k

$2 \cdot 10^{-8}$

R1D ,R2D ,RTD
k   k   k

$2 \cdot 10^{-11}$

10   Td   1000
k

6

EB , CRJ
 k   w

2

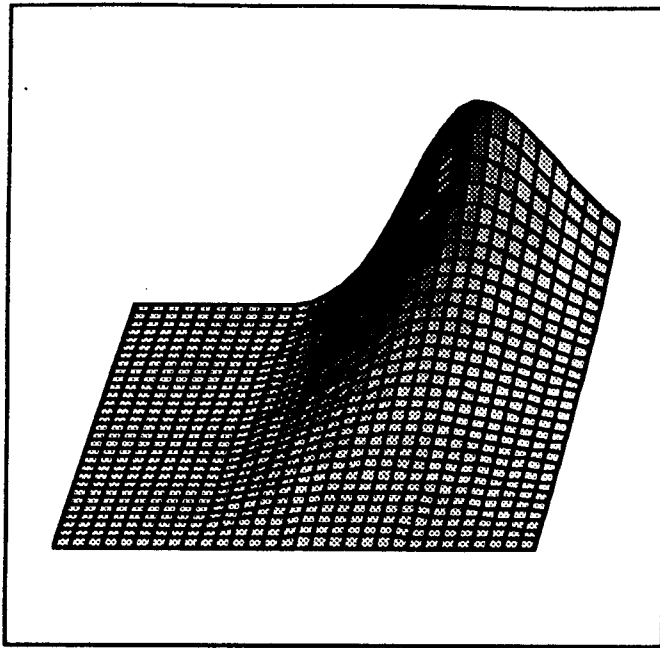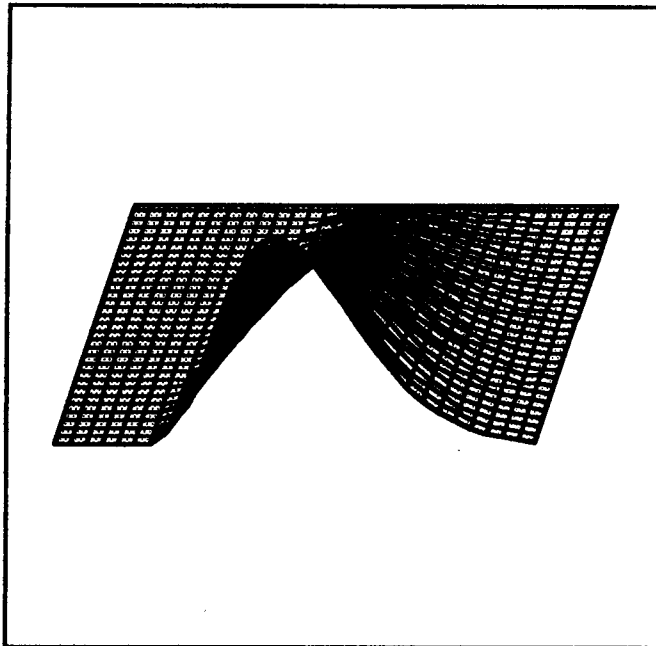50   Td , WT   200
             k   w
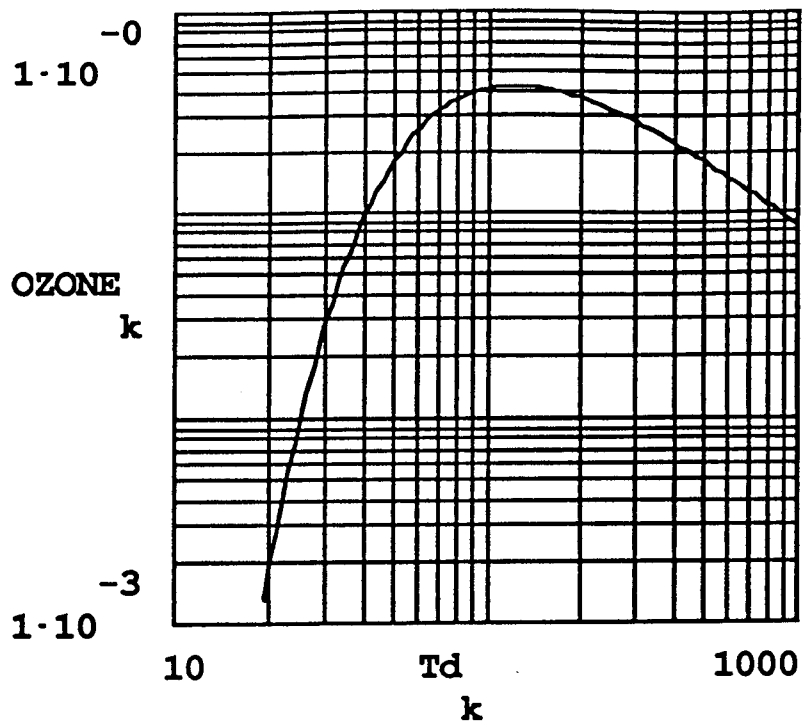
Electron average energy @ E/N in water vapor (line: Massey, 1969)

eV vs. Townsends
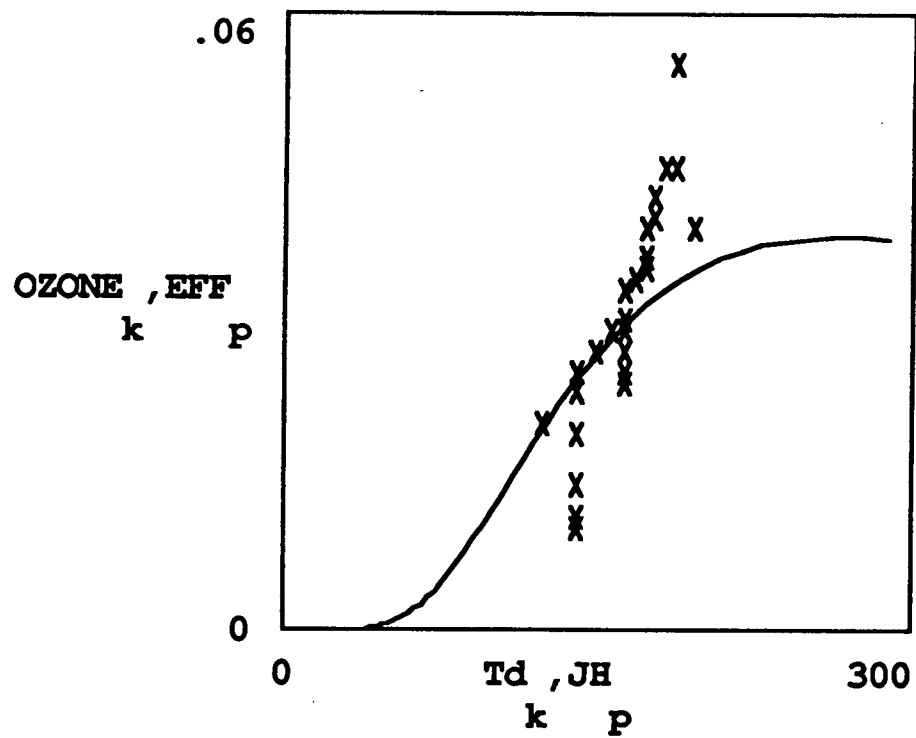
Ozone generation efficiency @ E/N in air: model and data

molecules/eV vs. Townsends

OZONE

WATER

Dissociation efficiency for oxygen & water

in mixtures between 100% dry air to 100% water vapor,
and 10 - 1000 Td.

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5) R. D. Hake, Jr. & A. V. Phelps, "Momentum-Transfer and Inelastic Collision Cross Sections for Electrons in O_2, CO, and CO_2," *Phys. Rev.*, Vol. 158, No. 1, (June 1967), pp 70 - 84.

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